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Layered metal organosulfides: hydrothermal synthesis, structure and magnetic behaviour of the spin-canted magnet Co(1,2-(O_2C)(S)C_6H_4)

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Reaction of cobalt(II) salts with the thiosalicylate dianion under hydrothermal conditions yields green lamellar Co((O_2C)(S)C_6H_4) which displays canted antiferromagnetism.

Recrystallisation of metal chalcogenides was among the earliest uses of superheated solution chemistry.[1] Since then there has been much interest in the preparation of new and more complex chalcogenides using superheated methanol,[2,3a] water,[2,3b] ammonia[4] and ethylenediamine.[5] In one case this has produced a cluster containing the methyl tellurolate (CH_3Te^-) anion,[3a] but there has been no successful synthesis of such a material starting from organochalcogenide anions. This is in contrast to the rapidly increasing number of solvothermally-prepared coordination solids based on oxygen[6] or nitrogen[7] donor ligands. We report here what we believe to be the first example of the hydrothermal preparation of a metal-organochalcogenide extended lattice.

Reaction of $CoCl_2 \cdot 6H_2O$ (101 mg, 0.424 mmol) with 1,2-(HO_2C)(HS)C_6H_4 (135 mg, 0.858 mmol) and KOH (1.68 ml of a 1 M solution in H_2O, 1.68 mmol) in water (10 ml) at 200 °C for 15 h followed by cooling to room temperature over 4 h yields very fine dark green plates in 73% yield. Larger crystals can be grown by the addition of a mineraliser such as NaBr (up to 5 g per reaction) and an identical product can also be obtained from the reaction of $Co(OH)_2$ with ligand salt. The phase purity of the bulk material was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study. X-Ray structural analysis† shows the compound to be monoclinic with an asymmetric unit consisting of one formula unit and therefore there is only one metal environment. The cobalt(II) ion is trigonal bipyramidal with an S_2O_3 donor set (Fig. 1) coming from four different ligands. Sulfur ligands occupy one of the axial and one of the equatorial sites whilst the O and S donor atoms of the one chelating ligand occupy apical (S) and equatorial (O) sites forming a six-membered ring. Each ligand is coordinated to four metal atoms with Co–S–Co and Co–O–Co angles of 97.38(3) and 101.90(8)°, respectively. The carboxylate bridge has a *syn–syn* configuration but with a dihedral angle of 49.8° between the Co1b–O1–C7 and Co1c–O2–C7 planes. The metal ions form the core of a ligand bilayer (Fig. 2) with the polar groups pointing inwards. The non-polar groups form an essentially flat surface hence the interlayer interactions will be relatively weak with no stabilising interdigitation as we have observed previously.[6d] It is therefore not surprising that the crystals form as very thin plates with hydrophobic surfaces.

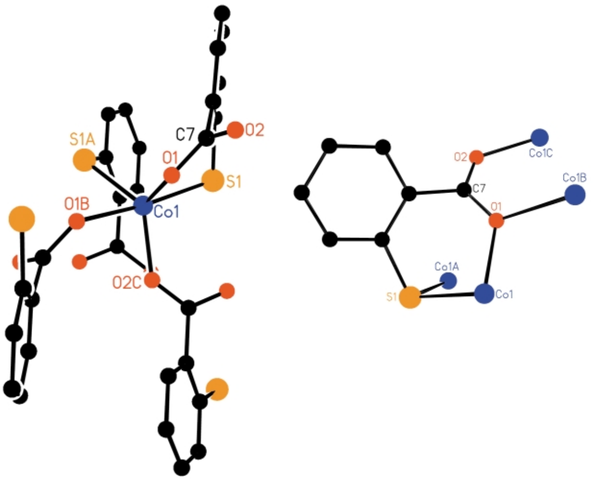

Fig. 1 The metal–ligand building blocks showing (a) all the ligands coordinated to one metal and (b) all the metals coordinated to one ligand. Selected bond distances (Å) and angles (°): Co1–O1 1.991(2), Co1–O1B 2.269(2), Co1–O2C 1.989(2), Co1–S1 2.3515(7), Co1–S1A 2.2996(7); O1–Co1–O1B 78.10(8), O1–Co1-O2C 102.66(8), O1–Co1–S1 92.05, O1–Co1–S1A 117.15(6), O1B–Co1–O2C 79.93(7), O1B–Co1–S1 169.82(5), O1B–Co1–S1A 83.69(5), O2C–Co1–S1 105.06(6) O2C–Co1–S1A 132.41(6), S1–Co1–S1A 98.77(3), Co1–S1–Co1A 97.38(3).

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Previous studies on the chemistry of the Co(II)/thiosalicylate system under ambient conditions yielded $Co(LH)_2(H_2O)_2$[8] or the Co(III)-containing ion[9] CoL_3^{3-}, hence the high temperature conditions have led to new chemistry. The small difference in ligand field stabilisation energies for different high spin Co(II) geometries means that many compounds may be prepared with this ion which do not exist for other transition metals. Reactions of other divalent ions with thiosalicylate salts do not yield any isostructural products, even in the case of Zn(II), which is the ion most likely to mimic Co(II) chemistry.

There are three types of ligand bridging which might give rise to magnetic superexchange interactions. In order of strength these are the Co–S–Co, Co–O–Co and Co–OCO–Co pathways. The sulfur-bridged superexchange lattice consists of isolated Co–S–Co–S chains parallel to the crystallographic *c* axis (Fig. 3). Addition of the single atom oxygen bridges increases the connectivity to give a rectangular net parallel to the *bc* plane. Inclusion of the magnetically less important OCO bridges gives a triangular sheet structure. Three-dimensional ordering is only possible at temperatures when the dipolar interaction between layers becomes important. Magnetisation measurements‡ show a steady increase in susceptibility with decreasing temperatures before a sharp anomaly centred at 9 K characteristic of long-

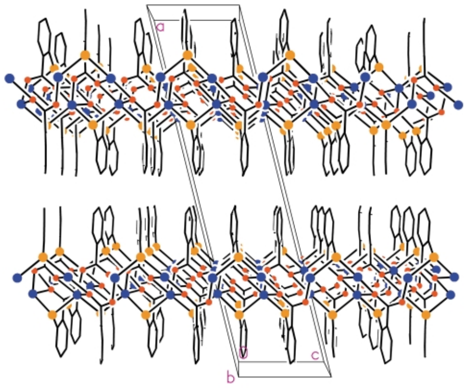

Fig. 2 Packing diagram parallel to [010].

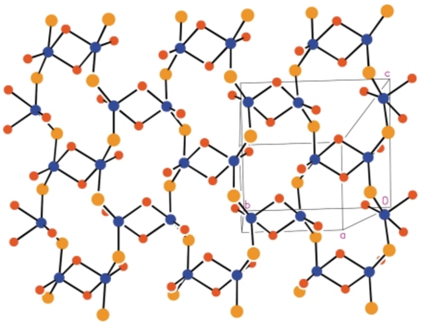

Fig. 3 The one-atom superexchange pathways within a single layer.

range ordering (Fig. 4). The magnetisation does not begin to saturate before 5 K but it is clear from its small magnitude that this is not a simple ferromagnetic state. As there is only one cobalt environment we may eliminate ferrimagnetism as a possibility and the source of the spontaneous magnetisation must therefore be a small degree of canting in an essentially antiferromagnetic system. This was confirmed by the variation of magnetisation with temperature for the ordered phase in different applied fields. The sample magnetisation is *higher* in *lower* measuring fields, which is characteristic of spin canting. Hysteresis measurements (Fig. 5) show a small coercive field of 45 G and that the sample magnetisation is not saturated at 5 T. The ferromagnetic interlayer interaction is a dipolar one across a relatively large gap of approximately 13 Å and is therefore small and only becomes significant at low temperatures. Canted antiferromagnetism is usually due to single ion anisotropy therefore high spin, octahedral Co(II) with large spin–orbit coupling due to its $^4T_{1g}$ ground term is a good candidate for this effect. Trigonal bipyramidal high spin Co(II) has a $^4A_1$ ground term and therefore lacks an orbital contribution to its magnetic moment and is also much less likely to undergo a significant degree of canting.

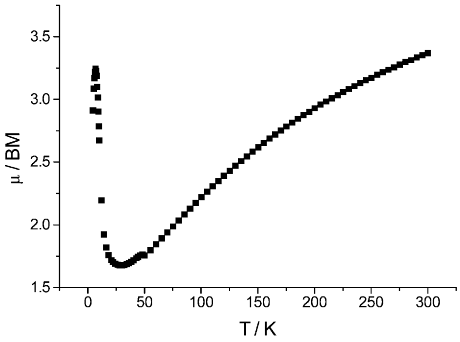

Fig. 4 The thermal evolution of the magnetic moment.

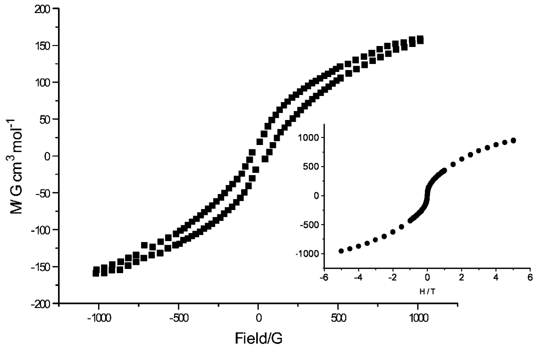

Fig. 5 Expansion of the magnetic hysteresis at 4.5 K in the low field region. Insert: field sweep between ±5 T.

Application of the Curie–Weiss law to the high temperature (> 100 K) data gives a remarkably large value of the Weiss constant ($\theta = -585(3)$ K) which is consistent with the low value of μ at room temperature compared to the spin only value of 3.87 μ_B. This is indicative of strong antiferromagnetic coupling as the lack of first-order angular momentum (*vide supra*) for the singlet ground term rules out the possibility that such a large deviation is due to single ion anisotropy. Comparison with typical values we have observed for $\theta \approx -50$ K in Co–O–Co bridged compounds with similar bridging angles shows that this strong interaction must be mediated by sulfur bridges. The greater covalency of Co–S bond *vs.* the Co–O bond leads to greater delocalisation of spin density and therefore stronger superexchange.[10] Since the Co–S superexchange lattice is comprised of isolated chains we should expect to see a broad maximum in the susceptibility *vs.* temperature graph coinciding with short-range ordering. Mean Field Theory is not a particularly good model for low dimensional systems but can give us a qualitative estimate of the exchange coupling; when it is combined with an expression[11] for the temperature at which the susceptibility maximum should occur we obtain the result $T_{max} = 1.9|\theta|$. The susceptibility maximum will therefore occur at a much higher temperature than could be measured.

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Notes and references

† *Crystal data*: $C_7H_4O_2SCo$, $M = 211.09$, monoclinic, space group $C2/c$, $a = 27.890(2)$, $b = 7.6926(6)$, $c = 6.7497(5)$ Å , $\beta = 103.895(2)°$, $V = 1405.8(2)$ Å^3, $Z = 8$, $D_c = 1.995$ g cm^{-3}, $\mu = 2.669$ mm^{-1}, $\lambda = 0.6904$ Å (Daresbury Station 9.8), crystal dimensions 0.12 × 0.10 × 0.01 mm. Total number of observed [$F^2 > 2\sigma(F^2)$] and independent reflections 1865, 1505 ($R_{int} = 0.0217$). Full-matrix least-squares on F^2 gives $R1 = 0.0385$ and $wR2 = 0.0974$.

CCDC reference number 176424. See http://www.rsc.org/suppdata/cc/b1/b111339a/ for crystallographic data in CIF or other electronic format.

‡ *Magnetisation measurements*: Data were recorded on a Quantum design MPMS-XL magnetometer. Temperature scans were recorded between 4.5 and 300 K using a cooling and measuring field of 500 G. Magnetisation hysteresis was studied between ±5 T at 5 K. Sample diamagnetism was corrected for by employing Pascal's constants.[10]

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